67. Homoconjugated Ketones with Extended Unsaturation: Wavelength-Selective, Regioselective, Diastereoselective, and Enantiospecific Photochemical Transformations of Methyl 7-Oxospiro[5.5]undeca-1,3- and -2,4-diene-2-carboxylate[1])

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Dedicated to Professor *Kurt Schaffner*

(19.I.93)

The title molecules were shown to photorearrange with remarkable selectivity. Wavelength variation steers the rearrangement modes, of which the [1,2]-acyl shift was found to be largely regioselective, diastereoselective, and enantiospecific. Chemical intercorrelation of products and mechanistic studies were carried out all along. The potential significance of these photochemical processes in selective synthetic schemes is discussed.

Introduction. – We recently described the interesting photochemical behaviour of a certain class of homoconjugated ketones with extended unsaturation, namely 5-acyl-cyclohexa-1,3-dienes. The spiro[5.5]undeca-1,3-dien-7-one system was found to be of particular interest and versatility [2], and an outline of its irradiation-induced transformations is given in *Scheme 1*. The wavelength selectivity is evident and remarkable: *i*) high-energy (254 nm) irradiation brings about an electrocyclic opening of the cyclohexadiene ring to the corresponding conjugated trienone, which is highly photoreactive and leads to a variety of secondary products; *ii*) at 300 nm, α-cleavage takes place, giving the corresponding 5-arylpentanal; *iii*) at both 300 and 350 nm, a ${}_{\sigma}2 + {}_{\pi}2$ oxa-di-π-methane[4]) rearrangement product of exclusive *trans*-configuration is obtained, and *iv*) sensitization triggers the formation of *ca.* 52 kcal/mol triplets which lead to the same ${}_{\sigma}2 + {}_{\pi}2$ ODPM rearrangement product, accompanied by its ${}_{\sigma}2 + {}_{\pi}4$ analogs in variably diastereoselective mixture of isomers, the composition of which is moderately directed by the position of the Me substituent. The last two modes (*iii* and *iv*) were by far the most interesting to us, for a variety of reasons, of both mechanistic and preparative nature.

We present now the detailed results of an investigation of 7-oxospiro[5.5]undeca-1,3-diene-2-carboxylate **1** as well as of 7-oxospiro[5.5]undeca-2,4-diene-2-carboxylate **6**, which was undertaken to examine the electronic effects of electron-withdrawing sub-

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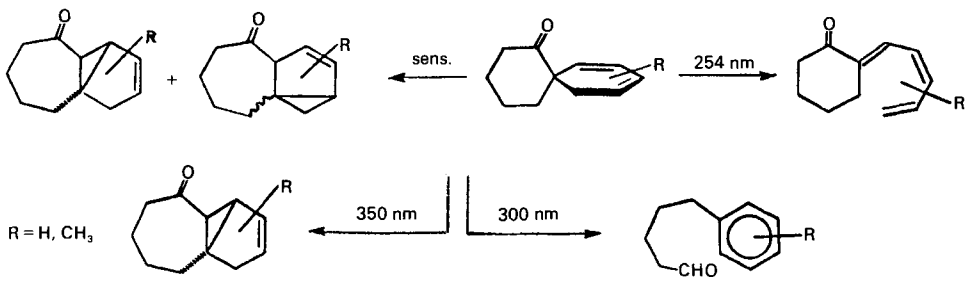
[4]) For reviews on the photochemistry of β,γ-unsaturated ketones, including the oxa-di-π-methane (ODPM) rearrangement, see [3].

Scheme 1



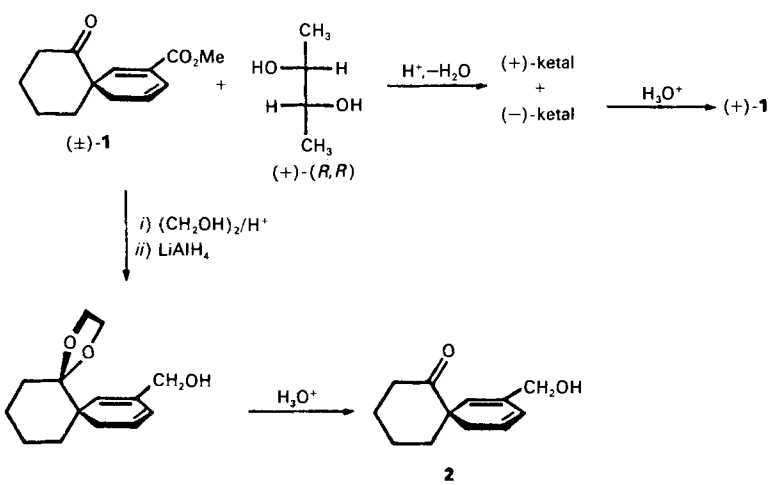
stituents on the photochemical behaviour of the system as well as to assess its generality and potential value for synthetic purposes.

Results and Discussion. – *Starting Materials.* The synthesis of racemic carboxylate (±)-**1** was described [5] [6]. However, we needed also the pure optically active form. Thus, ketalization of (±)-**1** with (+)-butane-2,3-diol yielded the diastereoisomer mixture of *trans*-dimethylethylene ketals (*Scheme 2*) which were separated by chromatography (silica gel). The (−)-ketal was hydrolysed to the optically pure ketone (+)-**1**, as shown by NMR measurements using a chiral shift reagent and within the precision limits of this method.

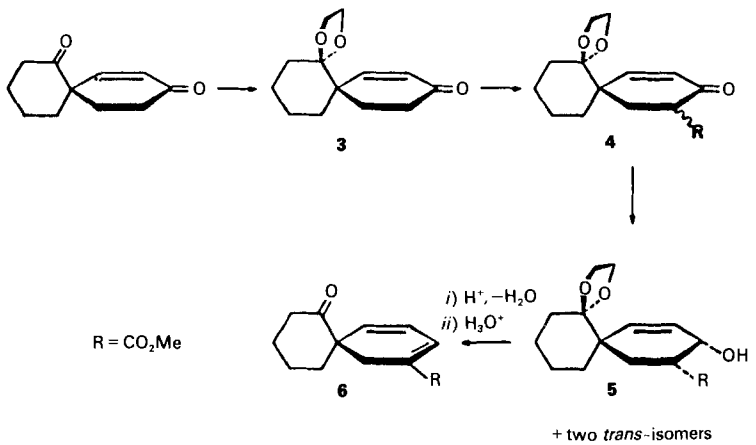
As elaborated below, the hydroxymethyl derivative **2** was also desired and hence prepared from (±)-**1** by deketalization of the previously reported ethylene ketal [5] (*Scheme 2*).

The carboxylate **6** was prepared from the known [7] [8] spiro[5.5]undec-7-ene-1,9-dione by selective ketalization (→**3**), followed by methoxycarbonylation [9] (→**4**; *Scheme 3*). $NaBH_4$ reduction of the diastereoisomer mixture **4** provided two *trans*-hydroxy esters and the *cis*-isomer **5**. The latter underwent readily acid-catalysed dehydration followed by deketalization to the desired 7-oxospiro[5.5]undeca-2,4-diene-2-carboxylate **6**.

Scheme 2



Scheme 3

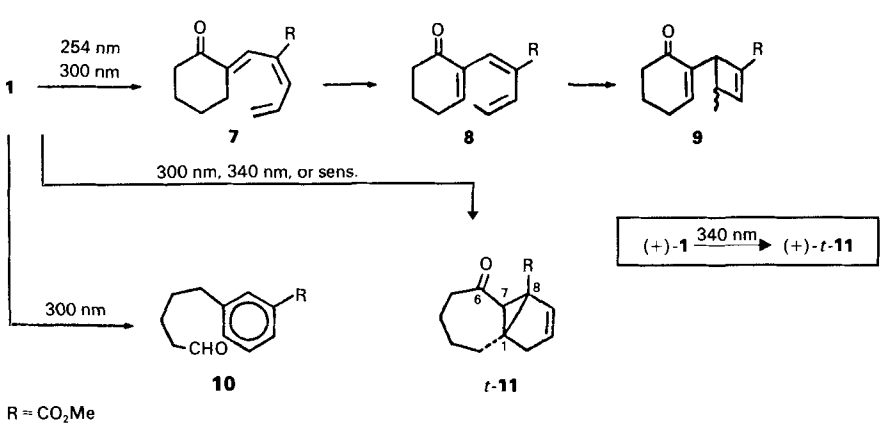


Photochemistry. Irradiation of **1** in MeCN gave the following results at the various wavelengths (*Scheme 4*):

i) At 254 nm, electrocyclic opening of the cyclohexadiene ring is the major primary process, but the expectedly labile, fully conjugated trienone **7** could be observed by ^{1}H-NMR only at low conversions in the irradiation mixture. It rapidly underwent a [1,7]-sigmatropic H-shift to give **8**. The latter was isolated in 25% yield along with its own butadiene→cyclobutene cyclization product **9** (35%). These products were identified on strength of their physical, in particular ^{1}H-NMR spectroscopic properties. In this reaction, *ca.* 5% of methyl 3-(4-formylbutyl)benzoate (**10**) were also isolated.

ii) At 300 nm, poor selectivity was observed. The reaction mixture contained products of three different primary processes (by ^{1}H-NMR), namely, the cyclobutene compound **9**

Scheme 4



[5]) For short preliminary communications of some of these results, see [4].

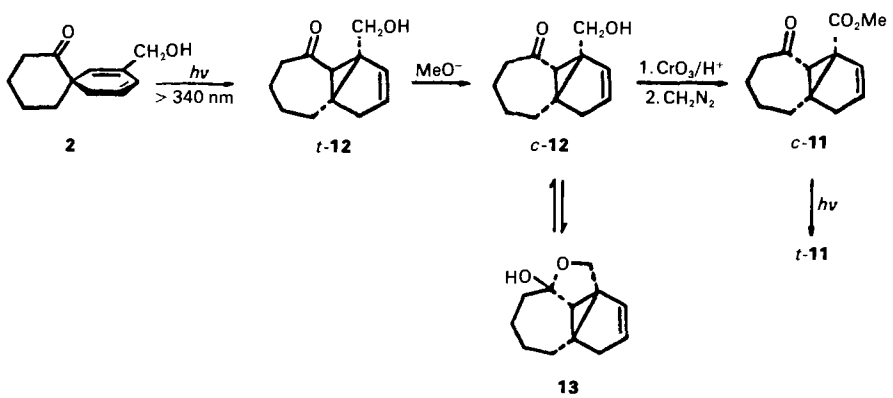
(25%) (formylbutyl)benzoate **10** (10%), and the [1,2]-acyl shift (ODPM) product *t*-**11** (60%; see below).

iii) At and above 340 nm (cut-off filter) and at *ca.* −10° (see below) an ODPM rearrangement of **1** took place to give exclusively and quantitatively 6-oxo-*trans*-tricyclo[5.4.0.0^{1,8}]undec-9-ene-8-carboxylate *t*-**11**, as identified by its spectroscopic data and chemical correlation (see below). A similar irradiation of the optically pure (+)-**1** gave optically pure (+)-*t*-**11** as shown by polarimetry and ^{1}H-NMR with chiral shift reagents. This proves the enantiospecificity of the photorearrangement.

iv) Sensitized irradiation of **1** in acetone as well as with other sensitizers gave again exclusively and quantitatively the $_\sigma2 + _\pi2$ *trans*-cycloaddition product *t*-**11**. We had expected [2] a less regioselective behaviour, *i.e.*, some $_\sigma2 + _\pi4$ rearrangement to occur under these conditions. This may indicate that the same excited triplet is attained in this system, by both direct and sensitized excitation, contrary to previously encountered behaviour [2].

The *cis*-isomer *c*-**11** could not be obtained, neither by photochemical means nor by chemical transformations (*vide infra*). Thus, we looked for an alternative synthesis. Preparative amounts of hydroxymethyl derivative **2** were irradiated at $\lambda > 340$ nm to give exclusively 8-(hydroxymethyl)-*trans*-tricyclo[5.4.0.0^{1,8}]undec-9-en-6-one (*t*-**12**) in 63% yield (*Scheme 5*). This was also the only product in sensitized irradiations. Compound *t*-**12** was readily isomerised under base catalysis to its *cis*-isomer *c*-**12** which, while stable as such in acidic medium, exists in and crystallizes from neutral solution as the internal hemiketal **13**. *Jones* oxidation of *c*-**12** followed by diazomethane esterification gave the elusive *cis*-ketoester *c*-**11**. Interestingly, on irradiation (300 nm), the latter rearranged readily to its *trans*-isomer *t*-**11**.

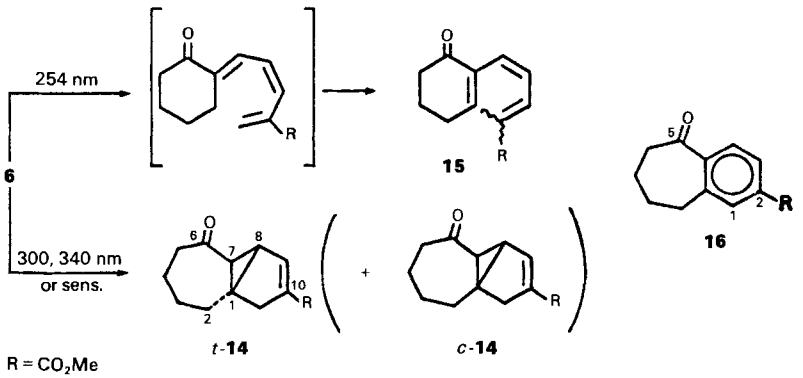
Scheme 5



Irradiations of carboxylate **6** in MeCN at various wavelengths gave the following results (*Scheme 6*):

i) At 254 nm, electrocyclic ring opening occurred followed by secondary processes, but only 12% could be chromatographically isolated and identified as a mixture of (*Z*/*E*)-isomers of trienone **15**. The rest had deteriorated (polymerised?) in the yellow reaction solution.

Scheme 6



ii) At 300 nm, **6** photorearranged sluggishly to give after 33 h, two isomeric compounds shown to be the ODPM rearrangement prodicts methyl 6-oxo-*trans*- and *cis*-tricyclo[5.4.0.0^{1,8}] undec-9-en-10-carboxylate (*t*-**14** (11%) and *c*-**14** (2%), resp.). The latter was, however, shown to be a secondary product (see below).

iii) At $\lambda > 340$ nm, the same two isomers *t*- and *c*-**14** were chromatographically isolated in 18 and 4% yield, respectively (*t*-**14**/*c*-**14** 5.5:1 in the crude reaction mixture (by ^{1}H-NMR)). Small amounts of the aromatic compound **16** were also obtained.

iv) Sensitized 350-nm irradiation with 2-acetonaphthone and ^{1}H-NMR examination of the reaction mixture showed, after 3.5 h, the presence of the two ODPM products *t*- and *c*-**14** in the ratio 4.5:1. Chromatography provided pure *t*-**14** (9%) and *c*-**14** (2%). Sensitization with acetone at 300 nm produced the same products in the ratio 1:1 (by ^{1}H-NMR, not isolated).

The reason for the poor yields in the photochemical conversions of **6** (in contrast to the straightforward behaviour of **1**) is not yet well understood, but is attributed to its higher proclivity for polymerization.

Mechanistic Photochemistry. The quantum yields ϕ of the ODPM photorearrangements were measured at 338 ± 6 nm for the disappearance of spirodienones and the formation of products: For **1**→*t*-**11**, ϕ (disapp., direct) = 0.11, ϕ (disapp., sensitized) = 0.35, ϕ (form., direct) = 0.07, and ϕ (form., sensitized) = 0.15; for **2**→*t*-**12**, ϕ (disapp., direct) = 0.06, ϕ (disapp., sensitized) = 0.33, ϕ (form., direct) = 0.02, and ϕ (form., sensitized) = 0.19.

A *Stern-Volmer* plot for the transformation **1**→*t*-**11** in MeCN using ferrocene as a quencher was linear up to $[Q] = 0.2$ and $\phi_0/\phi = 2.5$. Hence, a triplet excited state was concluded, and assuming diffusion-controlled quenching, $\tau \approx 1.5 \cdot 10^{-4}$ s.

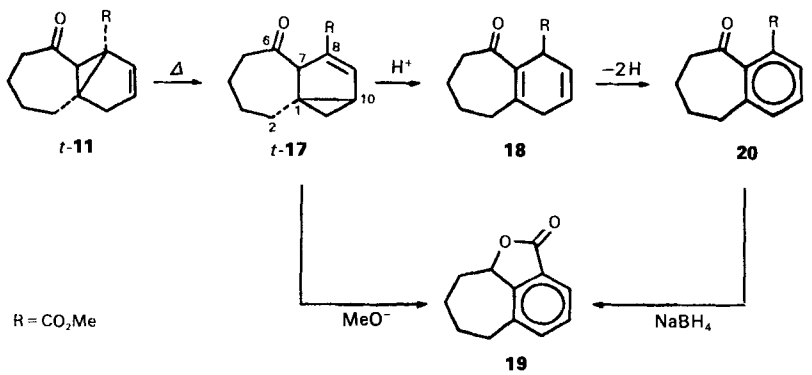
Sensitization of **1** and **6** was performed with a series of sensitizers with decreasing triplet energy (kcal/mol): acetone (78), xanthen-9-one (74), 2-acetonaphthone (59), 1-acetophenone (56), fluorenone (53), pyrene (49), and anthracene (42). It was found that **1**→*t*-**11** takes place even with pyrene, while **6**→*t*-**14** needs at least fluorenone. Hence, the triplet energies of **1** and **6** are evaluated as 48 and 52 kcal/mol, respectively.

Chemical Transformations of Photoproducts. The high regioselectively and diastereoselectivity in the described ODPM photorearrangements of **1** and (more moder-

ately) of **6** drove us to carry out a variety of experiments both to obtain the missing isomers of the photoproducts and to correlate between them.

Thermal isomerization of the photoproduct *t*-**11** (from **1**) readily occurred already at 50–60° in solution, in an essentially diastereospecific vinylcyclopropane rearrangement, to the isomeric 6-oxo-*trans*-tricyclo[5.4.0.0^{1,10}]undec-8-ene-8-carboxylate *t*-**17** (*Scheme 7*). The structure of this compound, besides being fully spectroscopically characterized, was proven by an X-ray diffraction analysis of its oxime (see preliminary communication [4b]). This actually provided also additional proof for the structural assignment of *t*-**11**, as well as strong support for the assignments in the entire series.

Scheme 7



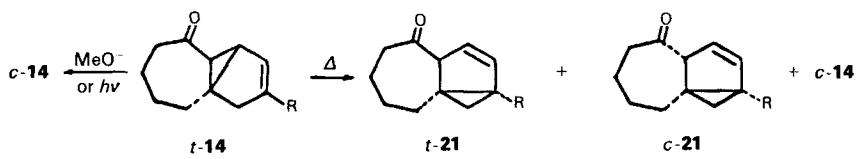
The first-order thermolysis *t*-**11**→*t*-**17** was kinetically investigated by ^{1}H-NMR at various temperatures in MeCN to give $\Delta H^{\neq} = 25.8$ kcal/mol and $\Delta S^{\neq} = 1.9$ e.u. These values were taken to indicate a diradical intermediate, rather than a zwitterionic or a concerted process. However, the observed stereospecificity demands a rather short lived, geometrically unrelaxed diradical.

The facile thermal process *t*-**11**→*t*-**17** caused us to perform the photorearrangement **1**→*t*-**11** at relatively low temperature, to keep it free of spurious traces of *t*-**17**.

Attempted base-catalysed *trans*→*cis* isomerization of *t*-**17** failed; instead, lactone **19** was isolated in 64% yield. Acid catalysis (CF_3COOH) brought about cyclopropane opening to **18** which readily underwent oxidation/aromatization to oxobenzocycloheptenecarboxylate (**20**). On $NaBH_4$ reduction of the latter, lactone **19** was again obtained. Any base treatment of *t*-**11** led also to **19**, apparently *via t*-**17**. We achieved, however, isolation of the *cis*-isomer *c*-**11** in the sequence of reactions described above (*Scheme 5*).

A similar series of reactions was performed on the photoproduct *t*-**14** of **6**. While acid treatment was ineffective, thermal, photochemical, and basic conditions brought about the transformations shown in *Scheme 8* Thus, thermolysis of pure *t*-**14** led to its disappearance in a first-order unimolecular reaction, with k (353 K) = 2.03 · 10^{-2} s^{-1}, as monitored by ^{1}H-NMR. The outcome after 14 h (complete conversion of *t*-**14**) was, however, a mixture of three isomers: the *cis*-isomer *c*-**14** and a mixture of the diastereoisomeric vinylcyclopropane rearrangement products *t*- and *c*-**21**. Evidently, the reaction is neither regio- nor stereospecific and is bound to occur *via* a diradical intermediate.

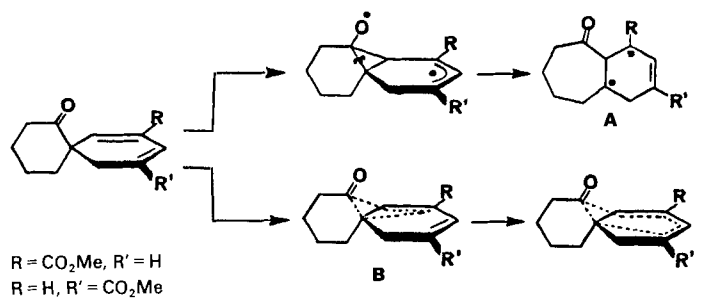
Scheme 8



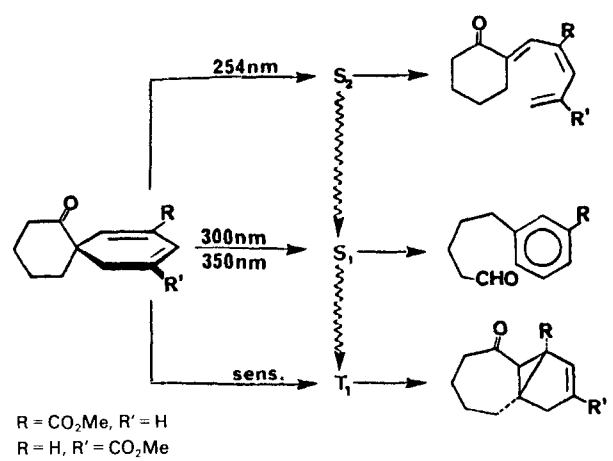
Notably, both direct and sensitized irradiation of *t*-**14** brought about a smooth photoisomerization to its *cis*-isomer *c*-**14**. A comparison of the rate of photolysis of **6** with that of *t*-**14** led to the unequivocal conclusion that the phototransformation **6**→*t*-**14** (see *Scheme 6* and details above) is actually diastereoselective and *c*-**14**, isolated there in minute amounts, is a secondary product.

There is, hence, complete regio- and diastereoselectivity in favour of the $_{\sigma}2 + _{\pi}2$ mode of the ODPM rearrangement, represented by either **A** or **B** in *Scheme 9*, in both the direct and sensitized phototransformations, pointing to a reasonable picture of excited states (*Scheme 10*). At this stage of mechanistic comprehension of these and previously [2]

Scheme 9



Scheme 10



described findings, however, it is difficult to pinpoint the exact reason for the differences in the behaviour of the COOMe-substituted oxospiro[5.5]undecadienes from the unsubstituted or Me-substituted ones [2]. A theoretical study of the entire problem is now nearing completion [10].

In conclusion, we have unravelled the photochemical behaviour of homoconjugated ketones of the spirodienone type, featuring electron-withdrawing COOMe substituents, the most interesting being the [1,2]-acyl shift or ODPM photorearrangement. It was found that the latter proceeds exclusively and in high yields at $\lambda > 300$ nm, in a regioselective, diastereoselective, and enantiospecific manner. We think that these, along with previous related results [2] [11], are of interest, beyond their basic chemical significance, in light of the recent studies which make use of the versatility of photochemical processes in syntheses of structurally intricate natural products [3g] [12]. The facile synthesis of starting materials and the otherwise difficultly attainable tricyclic systems and of their possible offsprings is bound to offer a new and attractive tool for synthetic purposes.

Experimental Part

1. *General.* All products were carefully purified by chromatographic methods. The pure products were fully characterized by spectroscopic methods, and selected compounds were subjected to high-resolution (HR) MS or X-ray diffraction analysis. No elemental analysis of the products was deemed necessary, since we dealt mostly with isomeric products in rearrangement processes. GLC: *Packard-427* instrument, capillary column *SE 30* (25 m); computing integrator from *Spectra-Physics* (system I). HPLC: *Water-Assoc.-M-4000-A* instrument, *Merck 7734* prepacked columns. CC = Column chromatography. M.p.: uncorrected. IR Spectra: *Perkin-Elmer-297* spectrophotometer; $\tilde{\nu}_{max}$ in cm^{-1}. UV Spectra: *Cary-219* spectrophotometer; λ_{max} (ε) in nm. NMR Spectra: *Bruker-WH-90* and *AM-360-WB* spectrometers; chemical shifts δ in ppm downfield from TMS, coupling constants J in Hz. MS: *DuPont-21-491-B* mass spectrometer; m/z (rel. %).

2. *Irradiations.* 2.1. *Preparative Irradiations. Rayonet* photoreactors (16 8-W lamps) or similar, locally built ones (32 lamps) using germicidal (254 ± 15 nm), cool-white (300 ± 30 nm) or black-light blue (350 nm) lamps, as well as a *Hanovia-679-A36* (450 W, medium-pressure Hg) lamp in immersion reactors. The following cut-off filters were used: *Corex* (for $\lambda > 280$ nm), or a soln. of NaBr (375 g) and $Pb(NO_3)_2$ (4 g) in H_2O (500 ml; for $\lambda > 340$ nm). General procedure: A *ca.* 0.1% soln. of spirodienone in purified MeCN (unless otherwise specified) was irradiated at the appropriate wavelength at *ca.* 35°, directly or in presence of a sensitizer, to optimum conversion. The soln. was then evaporated and the mixture analysed by TLC and subsequently chromatographed (silica gel) to obtain the pure products.

2.2. *Analytical and Mechanistic Irradiations. JASCO-CRM-FA* Spectroirradiator, at 257, 311, or 338 nm (band-width 2–15 nm, according to filters used), equipped with a photon counter. The latter was periodically calibrated by chemical actinometry (using mostly the *Aberchrome-540* actinometer). In sensitized reactions, it was made sure that the sensitizers absorb at least 95% of the relevant radiation.

Quantum yields were measured only at 311 nm ($1.24 \cdot 10^{-8}$ einstein/count) or 338 nm ($2.13 \cdot 10^{-8}$ einstein/count) with *ca.* 100 counts/min, using ^{1}H-NMR or GC monitoring.

All irradiations were performed on deoxygenated (N_2 or Ar) solns. in quartz (254 nm) or *Pyrex* (300 and 350 nm) vessels.

3. *Starting Materials and Preparative Procedures.* 3.1. *Methyl 7-Oxospiro[5.5]undeca-1,3-diene-2-carboxylate* (**1**) was prepared and described before [5] [6]. Full spectroscopic data: UV (cyclohexane): 279 (2600). IR (KBr): 3090, 3060, 2960, 2870, 1715, 1440. ^{1}H-NMR ($CDCl_3$): 6.98 (*s*, H–C(1)); 6.32 (*ddd*, J = 9.7, 3.6, 1.6, H–C(3)); 5.87 (*ddd*, J = 9.7, 4.9, 4.9, H–C(4)); 3.78 (*s*, MeO); 2.84–2.20 (*m*, 4 H); 2.0–1.5 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 210.2 (*s*); 165.8 (*s*); 137.2 (*d*); 128.4 (*s*); 126.3 (*d*); 120.4 (*d*); 51.8 (*q*); 50.4 (*s*); 38.4 (*t*); 37.0 (*t*); 30.0 (*t*); 27.8 (*t*); 20.5 (*t*).

3.2. *2-(Hydroxymethyl)spiro[5.5]undeca-1,3-dien-7-one* (**2**). The preparation of the ethylene ketal of **2** was described [5]. It was deketalized as follows: A suspension of silica gel (10 g) and 15% aq. H_2SO_4 soln. (3 ml) in

CH_2Cl_2 (20 ml) was stirred for 10 min. Then a soln. of the ketal (1.0 g, 4.24 mmol) in CH_2Cl_2 (2 ml) was added. The mixture was stirred vigourously at r.t. The reaction was complete after 16 h. The mixture was filtered and dried (K_2CO_3), the solvent evaporated, and the crude product purified by CC (SiO_2, CH_2Cl_2): **2** (0.51 g, 63%). UV (MeCN): 262 (2000), 300 (250). IR (neat): 3400, 3040, 2920, 2850, 1700, 1440. ^{1}H-NMR ($CDCl_3$): 5.83 (*s*, 2 H); 5.78 (*s*, 1 H); 4.10 (*s*, 2 H); 2.70 (*d*, *J* = 18, 1 H–C(5)); 2.60–2.20 (*m*, 3 H); 2.15 (*d*, *J* = 18, 1 H–C(5)); 2.05–1.55 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 212.0 (*s*); 136.0 (*s*); 126.7 (*d*); 122.8 (*d*); 122.7 (*d*); 65.0 (*t*); 49.6 (*s*); 38.3 (*t*); 38.2 (*t*); 31.5 (*t*); 28.0 (*t*). MS: 192 (M^+).

3.3. *Methyl 7-Oxospiro[5.5]undeca-2,4-diene-2-carboxylate* (**6**). *Spiro[5.5]undec-1-ene-3,7-dione 7,7-Ethylene Ketal* (**3**). Using a modified procedure [7] of [8], a benzene (250 ml) soln. of spiro[5.5]undec-1-en-3,7-dione (26.7 g, 0.15 mol), ethylene glycol (13 g, 0.20 mol), and TsOH (0.8 g) was refluxed under a *Dean-Stark* head for 2 h. The cooled mixture was washed with 3% aq. $NaHCO_3$ and sat. NaCl soln., dried ($MgSO_4$), and evaporated. The crude product was distilled (138–140°/0.03 Torr): **3** (22 g, 67%). IR ($CHCl_3$): 2950, 2900, 1715, 1690, 1460, 1100, 1040, 970. ^{1}H-NMR (CCl_4): 6.7 (*d*, *J* = 10.5, 1 H); 5.66 (*d*, *J* = 1.5, 1 H); 3.85 (br. *s*, 4 H); 2.57–1.17 (*m*, 12 H).

Methyl 7,7-(Ethylenedioxy)-3-oxospiro[5.5]undec-4-ene-2-carboxylate (**4**). Following a published procedure [9], a soln. of **3** (22 g, 0.1 mol) in benzene (150 ml) was added dropwise and with stirring during 75 min to a warm (60°) suspension of NaH (56%; 13 g, 0.25 mol) and dimethyl carbonate (54 g, 0.6 mol) in benzene (150 ml). The mixture was refluxed for 90 min, then cooled to 0°, acidified with AcOH (25 g, 0.415 mol), and poured onto an ice/HCl mixture. The org. layer was washed with H_2O, aq. $NaHCO_3$ soln. and sat. NaCl soln., dried ($MgSO_4$), and evaporated: crude **4** (22.6 g, 80%), 2 isomers as identified by NMR, but not isolated.

Methyl cis-*7,7-(Ethylenedioxy)-3-hydroxyspiro[5.5]undec-4-ene-2-carboxylate* (**5**). To a MeOH (5% H_2O) soln. of mixture **4** (22.6 g, 0.08 mol), $NaBH_4$ (3.7 g, 0.1 mol) was added during 90 min with stirring at r.t. The MeOH was evaporated and Et_2O added. The mixture was acidified (3% HCl soln.) to pH 6. The aq. layer was extracted 3 times with Et_2O. The combined extracts were washed with sat. NaCl soln., dried ($MgSO_4$), and evaporated. The crude product (22 g) contained 1 *cis*- and 2 *trans*-isomers. CC (silica gel) gave first the *cis*-isomer **5** (1.7 g, 7.5%), followed by a mixture of the 2 *trans*-isomers (5 g, 22%; not characterized). **5**: IR ($CHCl_3$): 3450, 2915, 1710. ^{1}H-NMR ($CDCl_3$): 5.95 (*d*, *J* = 2.6, 2 H); 4.38 (*d*, *J* = 2.6, 1 H); 3.93 (*m*, 4 H); 3.74 (*s*, 3 H); 2.60–2.66 (*dt*, *J* = 13.8, 3.5, 1 H); 2.13–2.60 (br. *s*, 1 H); 2.04–2.13 (*t*, *J* = 13.8, 1 H); 1.88–1.92 (*dd*, *J* = 13.8, 3.2, 1 H); 1.70–1.43 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 174.5 (*s*); 135.9 (*d*); 127.8 (*d*); 111.7 (2*d*); 65.3 (*t*); 64.9 (*t*); 63.7 (*q*); 51.8 (*s*); 44.4 (*s*); 42.2 (*t*); 33.3 (*t*); 30.7 (*t*); 23.2 (*t*); 20.6 (*t*). MS: 282 (M^+).

trans-Isomers (mixture): ^{1}H-NMR ($CDCl_3$): 5.75 (*d*, *J* = 2.4, 1 H); 5.85–5.68 (*m*, 3 H); 4.46 (*dt*, *J* = 9.5, 1.5, 1 H); 4.37 (*d*, *J* = 9.2, 1 H); 3.2 (*m*, 8 H); 3.75 (*s*, 3 H); 3.75 (*s*, 3 H); 3.07 (*dt*, *J* = 12.7, 3.3, 2 H); 2.96 (br. *s*, 2 H); 2.54 (*dt*, *J* = 12.7, 3.3, 1 H); 2.4 (*dd*, *J* = 14.2, 2.0, 1 H); 1.3–2.0 (16 H). MS: 282 (M^+).

Dehydration of **5** *to* **6**. A benzene soln. of **5** (0.1 g, 0.35 mmol) and TsOH (0.05 g) was refluxed under a *Dean-Stark* head for 6 h. The solvent was evaporated and the mixture chromatographed (silica gel): 30 mg (33%) of the ethylene ketal of **6**. A soln. of the ketal (0.4 g, 1.5 mmol) in CH_2Cl_2 (2 ml) was added to a suspension of silica gel (4 g) and 15% aq. H_2SO_4 soln. (1 ml) in CH_2Cl_2 (20 ml) and stirred for 48 h. The mixture was filtered, the soln. kept overnight on anh. K_2CO_3, after which the solvent was evaporated and the crude product purified by CC (SiO_2, CH_2Cl_2): **6** (0.2 g, 60%). UV (MeCN): 290 (6200). IR ($CHCl_3$): 2950, 1710, 1450, 1270, 920, 710. ^{1}H-NMR ($CDCl_3$): 6.94 (*dd*, *J* = 5.4, 2.1, 1 H); 6.20–6.23 (*d*, *J* = 9.6, 1 H); 6.10 (*dd*, *J* = 9.6, 5,4, 1 H); 3.78 (*s*, 3 H); 2.83 (*dd*, *J* = 17.6, 2.1, 1 H); 2.59 (*dd*, *J* = 17.6, 2.1, 1 H); 2.58–2.42 (*m*, 2 H); 2.00–1.69 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 211.5 (*s*); 167.4 (*s*); 135.5 (*d*); 131.4 (*d*); 126.5 (*s*); 124.0 (*d*); 51.7 (*q*); 50.5 (*s*); 38.4 (*t*); 37.3 (*t*); 29.6 (*t*); 27.7 (*t*); 20.5 (*t*). MS: 220 (M^+).

4. *Irradiations of* **1**. 4.1. *Direct Irradiations*. 4.1.1. *254 nm* (*Rayonet*, quartz, 500 mg in 330 ml of solvent). After irradiation (14 h, 90% conversion) and workup, the products were isolated by CC in the following order: **10** (5%, 25 mg), **9** (35%, 175 mg), and **8** (25%, 125 mg).

Methyl 2-[(Oxocyclohex-1-enyl)methylidene]pent-3-enoate (**8**). IR (neat): 1715, 1690. ^{1}H-NMR ($CDCl_3$): 7.24–7.44 (*m*, 2 H); 6.03 (*d*, *J* = 11.0, 1 H); 5.72 (*dq*, *J* = 11.0, 6.5, 1 H); 3.77 (*s*, 3 H); 1.6–2.5 (*m*, 6 H); 1.50 (*dd*, *J* = 6.5, 1.3, 3 H). MS: 220 (M^+).

Methyl 3-Methyl-4-(6-oxocyclohex-1-enyl)cyclobut-1-ene-1-carboxylate (**9**). UV (MeCN): 245. IR (neat): 1715, 1690. ^{1}H-NMR ($CDCl_3$): 7.44 (*m*, 1 H); 7.32 (*m*, 1 H); 3.79 (*s*, 3 H); 3.75 (*m*, 1 H); 1.6–2.9 (*m*, 7 H); 0.86 (*d*, *J* = 6.9, 3 H). MS: 220 (M^+).

Methyl 3-(4-Formylbutyl)benzoate (**10**). IR (neat): 3020, 2980, 2975, 2880, 1725, 1450, 1300, 1220, 1100, 1010, 920. ^{1}H-NMR ($CDCl_3$): 9.75 (*t*, *J* = 2.0, 1 H); 7.85 (*m*, 2 H); 7.38 (*m*, 2 H); 3.91 (*s*, 3 H); 2.2–2.8 (*m*, 4 H); 1.5–2.0 (*m*, 4 H). MS: 220 (M^+).

4.1.2. *300 nm* (*Rayonet, Pyrex*, 110 mg in 100 ml of cyclohexane). After 48 h, the solvent was removed and the residue examined by ^{1}H-NMR: **10**/**9**/*t*-**11** (see below) 1:2.5:6.

4.1.3. *340 nm (Rayonet, Pyrex,* 220 mg in 100 ml of solvent). After irradiation for 40 h at −10° (cooled by circulating cold MeOH in outer jacket), the solvent was removed at 0° *in vacuo*: *methyl 6-oxo-*trans-*tricyclo[5.4.0.0^{1,8}]undec-9-ene-8-carboxylate* (*t*-**11**; quant.). IR (neat): 2920, 2860, 1700, 1435, 1265, 1165, 1130, 1065, 1030, 1000, 960, 920. ^{1}H-NMR ($CDCl_3$): 6.10 (*ddd, J* = 6.0, 2.0, 2.0, H–C(9)); 5.59 (*ddd, J* = 6.0, 2.5, 2.5, H–C(10)); 3.75 (*s*, 3 H); 3.15 (*s*, H–C(7)); 2.2–2.7 (*m*, 4 H); 1.6–2.1 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 200.2 (*s*); 169.3 (*s*); 128.9 (*d*); 126.7 (*d*); 51.7 (*q*); 49.8 (*d*); 43.5 (*s*); 42.5 (*t*); 41.9 (*t*); 38.3 (*s*); 32.8 (*t*); 28.2 (*t*); 24.0 (*t*). MS: 220 (M^+).

4.2. *Sensitized Irradiations.* Solns. of **1** (55 mg) in MeCN (100 ml) were irradiated at 350 nm (*Rayonet, Pyrex*) for 15 min, in the absence or presence of a sensitizer at concentrations which caused total absorbance (monitoring by ^{1}H-NMR). The solvent was then removed: only *t*-**11** was observed. Conversions: 50% without sensitizer, 100% with 2-acetophenone (180 mg/100 ml), 100% with 1-acetophenone (180 mg/100 ml), 100% with pyrene (200 mg/100 ml), and 0% with anthracene (50 mg/100 ml).

Irradiation in acetone (as solvent and sensitizer) under similar conditions gave also *t*-**11** quantitatively.

5. *Irradiations of* **2**. 5.1. *Direct Irradiation.* 5.1.1. *350 nm (Rayonet, Pyrex,* 96 mg in 100 ml of solvent). After 24 h, the solvent was removed and the residue chromatographed (silica gel): exclusively *8-(hydroxymethyl)-*trans-*tricyclo[5.4.0.0^{1,8}]undec-9-en-6-one* (*t*-**12**; 60 mg, 63%). IR (neat): 3400, 3060, 2930, 2860, 1690, 1440, 1400, 1220, 1190, 1160, 1140, 1090, 1030. ^{1}H-NMR ($CDCl_3$): 5.9 (*ddd, J* = 6.0, 2.0, 2.0, 1 H); 5.45 (*ddd, J* = 6.0, 2.0, 2.0, 1 H); 3.82 (*d, J* = 12, 1 H); 3.55 (*d, J* = 12, 1 H); 1.3–2.8 (*m*, 12 H). MS: 192 (M^+).

5.2. *Sensitized Irradiation.* 5.2.1. *350 nm (Rayonet, Pyrex,* 1.92 g in 500 ml of MeCN containing 1 g of 2-acetonaphthone). After 24 h, the solvent was evaporated and the residue chromatographed (silica gel): *t*-**12** (1.15 g, 60%).

6. *Irradiations of* **6**. 6.1. *Direct Irradiations.* 6.1.1. *254 nm (Rayonet,* quartz, 100 mg in 100 ml of solvent). After 40 min (yellow soln.), the solvent was evaporated and the residue chromatographed: *methyl 2-methyl-5-(6-oxocyclohex-1-enyl)penta-2,4-dienoate* (**15**; 12 mg, 12%; 2 diastereoisomers not separated). ^{1}H-NMR ($CDCl_3$): 6.0–7.4 (*m*, 8 H); 3.77 (*s*, 3 H); 3.76 (*s*, 3 H); 0.16–2.7 (*m*, 11 H). MS: 220 (M^+).

6.1.2. *300 nm (Rayonet, Pyrex,* 92 mg in 100 ml of solvent). After 33 h, the solvent was evaporated and the residue chromatographed (silica gel): *t*-**14** (10 mg, 11%) and *c*-**14** (2 mg, 2%).

*Methyl 6-Oxo-*trans-*tricyclo[5.4.0.0^{1,8}]undec-9-ene-10-carboxylate* (*t*-**14**): IR ($CHCl_3$): 2950, 1700, 1260, 1080, 1440, 1260, 1200, 1100. UV (MeCN): 245 (5800). ^{1}H-NMR ($CDCl_3$): 6.90 (*dd, J* = 4.0, 2.1, 1 H); 2.73 (*d, J* = 18.5, 1 H); 2.70 (*dd, J* = 6.3, 3.0, 1 H); 2.52 (*dd, J* = 8.7, 3.6, 2 H); 2.45 (*dt, J* = 14.0, 2.5, 1 H); 2.34 (*d, J* = 6.3, 1 H); 2.21 (*dt, J* = 12.6, 3.0, 1 H); 2.10 (*m*, 1 H); 1.89 (*m*, 2 H); 1.69 (*m*, 1 H); 1.46 (*dt, J* = 12.6, 4.4, 1 H). ^{13}C-NMR ($CDCl_3$): 201.3 (*s*); 164.4 (*s*); 140.6 (*d*); 133.9 (*s*); 51.4 (*q*); 42.6 (*t*); 41.6 (*d*); 30.6 (*d*); 37.5 (*t*); 37.2 (*t*); 35.0 (*s*); 29.1 (*t*); 24.9 (*t*). MS: 220 (M^+).

*Methyl 6-Oxo-*cis-*tricyclo[5.4.0.0^{1,8}]undec-9-ene-10-carboxylate* (*c*-**14**): IR ($CHCl_3$): 2950, 1700, 1660, 1420, 1260, 1100, 800. ^{1}H-NMR ($CDCl_3$): 6.94 (*dd, J* = 4.0, 1.8, 1 H); 2.92 (*dt, J* = 18.3, 2.4, 1 H); 2.75 (*dd, J* = 18.3, 1.8, 1 H); 2.72 (*dd, J* = 5.5, 2.7, 1 H); 2.45 (*m*, 1 H); 2.40 (*dt, J* = 11.7, 4.0, 1 H); 2.21 (*dt, J* = 14.6, 2.7, 1 H); 1.25–1.92 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 209.3 (*s*); 165.2 (*s*); 144.9 (*d*); 134.6 (*s*); 51.5 (*q*); 48.5 (*d*); 44.1 (*t*); 42.4 (*t*); 37.1 (*d*); 36.2 (*s*); 33.2 (*t*); 26.6 (*t*); 24.9 (*t*). MS: 220 (M^+).

6.1.3. *> 340 nm (Rayonet, Pyrex,* 100 mg in 100 ml of solvent). After 5 h, the solvent was removed and the residue chromatographed: *t*-**14** (18 mg, 18%), *c*-**14** (4 mg, 4%), and small amount of *methyl 6,7,8,9-tetrahydro-5-oxo-5*H*-benzocycloheptene-2-carboxylate* (**16**). IR ($CHCl_3$): 2950, 1710, 1680, 1440, 1400, 1280, 1240, 1100, 980. UV (MeCN): 294 (18200), 255 (30800). ^{1}H-NMR ($CDCl_3$): 7.96 (*dd, J* = 8.0, 1.5, 1 H); 7.92 (*d, J* = 1.5, 1 H); 7.76 (*d, J* = 8.0, 1 H); 3.97 (*s*, 3 H); 3.76 (*d, J* = 12.0, 1 H); 3.0 (*t, J* = 6.6, 2 H); 2.77 (*d, J* = 12.0, 1 H); 2.78 (*t, J* = 2.0, 1 H); 1.9 (*q, J* = 6.6, 1 H); 1.8 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 206.1 (*s*); 166.6 (*s*); 142.5 (*s*); 141.1 (*s*); 133.1 (*s*); 130.9 (*d*); 128.6 (*d*); 127.7 (*d*); 52.4 (*q*); 40.8 (*t*); 32.4 (*t*); 25.1 (*t*); 20.9 (*t*). MS: 218 (M^+).

6.2. *Sensitized Irradiations.* 6.2.1. *300 nm (Rayonet, Pyrex,* 50 mg in 100 ml of acetone). After 21 h, the solvent was removed and the residue purified by CC: *t*-**14**/*c*-**14** 1:1 (by ^{1}H-NMR; not isolated separately).

6.2.2. *> 340 nm (Rayonet, Pyrex,* filter soln., 95 mg in 100 ml of MeCN containing 2-acetonaphthone (400 mg)). After 3.5 h, the solvent was removed and the residue chromatographed: *t*-**14** (8 mg, 8.5%) and *c*-**14** (2 mg, 2.1%).

In anal. runs under similar conditions, 22.5 mg of **6** in 40 ml of MeCN in the absence or presence of a sensitizer were irradiated for 45 min. The solvent was removed and the conversion to **14** determined by ^{1}H-NMR. Conversions: 10% without sensitizer, 28% with 2-acetophenone (150 mg/100 ml), 20% with fluorenone (115 mg/100 ml), and 0% with pyrene (250 mg/100 ml).

7. *Thermal Transformations.* 7.1. *Methyl 6-Oxo-*trans-*tricyclo[5.4.0.0^{1,10}]undec-8-ene-8-carboxylate* (*t*-**17**) Solns. of photoproduct *t*-**11** (25 mg, 0.25 mmol) in MeCN (0.5 ml) were heated in NMR tubes at various temp. up

to 62°. The reaction was followed by ^{1}H-NMR until completion, and finally *t*-**17** was isolated. IR (neat): 2920, 2850, 1700, 1435, 1340, 1310, 1290, 1265, 1200, 1160, 1130, 1100, 1065, 1050, 960. ^{1}H-NMR ($CDCl_3$): 6.97 (*dd, J* = 2.5, 1.2, H–C(9)); 4.42 (br. *s*, H–C(7)); 3.68 (*s*, 3 H); 1.2–2.7 (*m*, 9 H); 1.8 (*ddd, J* = 7.9, 3.0, 2.5, H–C(10)); 0.71 (*dd, J* = 7.9, 4.2, 1 H–C(11)); 0.48 (*dd, J* = 4.2, 3.0, 1 H–C(11)). ^{13}C-NMR: 208.5 (*s*); 164.5 (*s*); 149.1 (*d*); 132.6 (*s*); 61.2 (*d*); 51.2 (*q*); 42.7 (*t*); 36.1 (*d*); 29.7 (*s*); 27.7 (*t*); 26.8 (*t*); 23.1 (*t*); 20.3 (*t*). MS: 220 (M^+).

The oxime of *t*-**17** (obtained with $NH_2OH \cdot HCl$ and NaOAc in H_2O in a standard procedure; m.p. 155° (from Et_2O); MS: 186 (M^+)) was subjected to X-ray diffraction (see structural analysis in [4b]).

A plot of ln a_0/a_t was made for each of the above thermal isomerization runs, and good first-order behaviour was observed, with k(345 K) = $8.4 \cdot 10^{-4}$, k(335 K) = $3.1 \cdot 10^{-4}$, k(325 K) = $8.5 \cdot 10^{-5}$, k(316 K) = $2.5 \cdot 10^{-5}$, and k(296 K) = $1.2 \cdot 10^{-6}$ s^{-1}. Hence, ln (k/T) *vs.* $1/T$ gave $\Delta H^{\neq}$ = 25.8 kcal/mol and $\Delta S^{\neq}$ = 1.9 cal/deg.

8. *Base-Catalyzed Transformations.* 8.1. *6,7,8,9-Tetrahydro-5*H*-benzocycloheptene-4,5-carbolactone* (**19**). The thermal rearrangement product *t*-**17** (110 mg) was stirred in 0.3N NaOMe/MeOH (3 ml) for 15 min. After evaporation, H_2O was added and the mixture extracted with $CHCl_3$. The soln. was dried ($MgSO_4$) and evaporated and the residue recrystallized from petroleum ether: **19** (60 mg, 64%). M.p. 84–86° UV (MeCN): 286 (1950), 278 (1850), 231 (8500). IR (KBr): 3020, 2940, 2860, 1760, 1490, 1450, 1365, 1310, 1280, 1265, 1090, 1060, 1010, 875. ^{1}H-NMR ($CDCl_3$): 7.69 (*m*, 1 H); 7.38 (*m*, 2 H); 5.34 (*dd, J* = 11.6, 3.7, 1 H); 1.4–2.9 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 170.7 (*s*); 150.8 (*s*); 138.3 (*s*); 133.4 (*d*); 129.1 (*d*); 125.8 (*s*); 123.1 (*d*); 82.6 (*d*); 35.3 (*t*); 33.0 (*t*); 27.9 (*t*); 27.7 (*t*). MS: 188 (M^+).

8.2. *8-(Hydroxymethyl)-*trans*-tricyclo[5.4.0.0^{1,8}]undec-9-en-6-one Internal Hemiketal* (**13**). A soln. of *t*-**12** (0.9 g, 4.7 mmol) in dry MeOH (5 ml) was added dropwise to a MeOH soln. of 1N NaOMe (15 ml) and then stirred at r.t. for 3 h under N_2. The solvent was evaporated, Et_2O was added, and the org. soln. washed with H_2O and then dried ($MgSO_4$). After filtration and evaporation, **13** (650 mg, 72%) was recrystallized from Et_2O. M.p. 120–122°. IR (KBr): 3400, 3070, 2900, 2860, 2830, 1430, 1350, 1330, 1290, 1260, 1220, 1200, 1180, 1150, 1130, 1110, 1080, 1050, 990, 970. ^{1}H-NMR ((D_5)pyridine): 5.56 (*ddd, J* = 5.7, 3.0, 2.5, 1 H); 5.16 (*ddd, J* = 5.7, 3.0, 2.0, 1 H); 4.80 (*s*, OH); 4.37 (*d, J* = 8.6, 1 H); 3.79 (*d, J* = 8.6, 1 H); 2.6–1.2 (10 H); 1.15 (*s*, 1 H). MS: 192 (M^+).

To a soln. of **13** (50 mg) in $CDCl_3$ in an NMR tube, a drop of CF_3COOH was added, to yield immediately and cleanly a soln. of *8-(hydroxymethyl)-*cis*-tricyclo[5.4.0.0^{1,8}]undec-9-en-6-one* (*c*-**12**). ^{1}H-NMR ($CDCl_3$/CF_3COOH): 6.0 (*ddd, J* = 5.0, 2.0, 2.0, 1 H); 5.52 (*ddd, J* = 5.5, 2.0, 2.0, 1 H); 4.1 (*d, J* = 12.0, 1 H); 3.65 (*d, J* = 12.0, 1 H); 2.9–1.2 (12 H).

An acetone (5 ml) soln. of the above *c*-**12**/**13** equilibrium mixture (96 mg, 0.5 mmol) was treated with *Jones'* reagent (0.5 ml) with stirring at 0° for 1 h. The solvent was evaporated, Et_2O was added, and the soln. washed with H_2O, dried ($MgSO_4$), and ice-cooled. Then an Et_2O soln. of diazomethane was added with stirring until persistence of the yellow colour. After standing 15 min, the mixture was evaporated and the residue chromatographed (silica gel): *methyl 6-oxo-*cis*-tricyclo[5.4.0.0^{1,8}]undec-9-ene-8-carboxylate* (*c*-**11**; 60 mg, 55%). UV (MeCN): 285 (50). IR (neat): 3080, 2940, 2870, 1725, 1710, 1460, 1360, 1270, 1200, 1170, 1140, 1060, 1000. ^{1}H-NMR ($CDCl_3$): 6.16 (*ddd, J* = 5.8, 2.2, 2.2, 1 H); 5.57 (*ddd, J* = 5.8, 2.2, 2.2, 1 H); 3.71 (*s*, 3 H); 2.80–2.40 (*m*, 4 H); 2.80–2.40 (*m*, 2 H); 2.79 (*ddd, J* = 17.4, 2.2, 2.2, 1 H); 2.52 (*ddd, J* = 17.4, 2.2, 2.2, 1 H); 2.40–1.65 (*m*, 6 H); 1.71 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 205.4 (*s*); 169.8 (*s*); 133.5 (*d*); 128.8 (*d*); 51.8 (*q*); 49.2 (*d*); 45.8 (*s*); 42.8 (*t*); 42.2 (*t*); 38.4 (*s*); 27.0 (*t*); 25.0 (*t*); 22.0 (*t*). MS: 220 (M^+).

A soln. of *c*-**11** (22 mg, 0.1 mmol) in acetone (20 ml) was irradiated (300 nm) for 100 h (50% conversion). At sub-zero temp., *t*-**11** was observed. At reactor temp. (*ca.* 40°), the thermal isomerization product *t*-**17** was isolated (see *6.1*).

8.3. *Isomerization* t-**14**→c-**14**. 8.3.1. Na (3 mg) was dissolved in CD_3OD (0.4 ml) in an NMR tube and *t*-**14** (3 mg) added. After 4 h, clean and full conversion to *c*-**14** had taken place as shown by ^{1}H-NMR (*cf. 6.1.2*).

8.3.2. To a suspension of basic alumina (0.25 mg) in $CDCl_3$ (1 ml), *t*-**14** (5 mg) was added and stirred at r.t. for 4 days (^{1}H-NMR monitoring). After 12 h, *t*-**14**/*c*-**14** was 6.5, and after 4 days it had decreased to 5.7.

9. *Acid-Catalyzed Transformations.* A soln. of *t*-**17** (1.1 g) in $CHCl_3$ (10 ml) containing CF_3COOH (1 ml) was stirred for 12 h. The soln. was neutralized over anh. K_2CO_3. After filtration and evaporation of the filtrate, the residue was chromatographed: *methyl 4,5,6,7,8,9-hexahydro-9-oxo-1*H*-benzocycloheptene-1-carboxylate* (**18**; 1.0 g, 90%). IR (neat): 3040, 2940, 2860, 1720, 1650, 1430, 1325, 1290, 1260, 1200, 1170, 1100, 990, 910. ^{1}H-NMR ($CDCl_3$): 5.83 (*m*, 2 H); 4.22 (*m*, 1 H); 3.67 (*s*, 3 H); 2.94 (*m*, 2 H); 2.62 (*m*, 2 H); 2.41 (*m*, 2 H); 1.81 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 204.8 (*s*); 173.1 (*s*); 150.2 (*s*); 131.5 (*s*); 125.1 (*d*); 123.1 (*d*); 52.2 (*q*); 43.7 (*d*); 41.4 (*t*); 34.6 (*t*); 32.8 (*t*); 23.9 (*t*); 20.6 (*t*). MS: 220 (M^+).

A $CHCl_3$ soln. of **18** (220 mg) was left standing for 3 months. Then CC gave *methyl 6,7,8,9-tetrahydro-9-oxo-5*H*-benzocycloheptene-1-carboxylate* (**20**; 130 mg, 60%). IR (neat): 3080, 3020, 2950, 2870, 1730, 1705, 1600, 1440,

1290, 1200, 1140, 1010, 960, 950, 910. ^{1}H-NMR ($CDCl_3$): 7.73 (*d*, *J* = 7.5, 1 H); 7.2–7.5 (*m*, 2 H); 3.85 (*s*, 3 H); 2.6–2.9 (*m*, 4 H); 1.8–2.0 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 209.8 (*s*); 167.9 (*s*); 143.9 (*s*); 137.6 (*s*); 132.5 (*d*); 129.3 (*d*); 128.9 (*s*); 127.7 (*d*); 52.3 (*q*); 42.0 (*t*); 33.1 (*t*); 26.3 (*t*); 24.8 (*t*). MS: 218 (M^+).

10. *Further Preparations of Lactone* **19**. 10.1. To a soln. of **18** (1.1 g, 5 mmol) in MeOH (10 ml), a soln. of 1N MeONa (10 ml) was added. After 15 min of stirring at r.t., the mixture was evaporated, and $CHCl_3$ was added. The soln. was washed with H_2O, dried ($MgSO_4$), and evaporated and the residue chromatographed: **19** (280 mg, 30%) which was recrystallized from petroleum ether.

10.2. To a soln. of **20** (100 mg) in MeOH (10 ml), $NaBH_4$ (40 mg) was added in small portions while stirring. After 2 h, the solvent was removed and $CHCl_3$ added (20 ml). The soln. was washed with H_2O, dried ($MgSO_4$), and evaporated: **19** (50 mg, 58%).

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